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Growth of Hg-Based Cuprate Films on Lanthanum-Aluminate Using Fast-Temperature Ramping Hg-Vapor Annealing

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Fast temperature ramping Hg-vapor annealing (FTRA) process has been used for growth of superconducting Hg-based cuprate thin films on (100) $LaAlO_3$ substrates. The film/substrate interface chemical reactions and the formation of $CaHgO_2$ impurity phase have been effectively reduced with adoption of FTRA process. Zero-resistance superconducting transition temperature of 128 K and critical current density of up to 1.4×10^6 A/cm^2 at 77 K and 2.5×10^5 A/cm^2 at 110 K and zero field have been obtained.

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GROWTH OF Hg-BASED CUPRATE FILMS ON LANTHANUM-ALUMINATE USING FAST TEMPERATURE RAMPING Hg-VAPOR ANNEALING

INTRODUCTION

Since the discovery of superconductivity above 130 K [1,2] in Hg-based high temperature superconductors ($HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$, n=1,2,3), there have been many efforts to fabricate high-quality thin films of these new materials for electronic device applications and fundamental studies [3-6]. In spite of difficulties of forming superconducting phases due to the high volatility of Hg and various contamination problems, advances have been achieved recently in growth of epitaxial Hg-based cuprate thin films on (100) $SrTiO_3$ substrates [3-6]. Superconducting transition temperatures (T_c's) above 130 K have been obtained on *c*-oriented $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) thin films [6]. Superconducting critical current densities (J_c's) of these films are over 2 MA/cm^2 at 5 K and 5 Tesla magnetic field and are larger than 0.1 MA/cm^2 at 110 K and zero field. Hg-based cuprate thin films are therefore very promising for various electronic device applications.

Only $SrTiO_3$ substrates have been used previously for the growth of the Hg-based cuprate thin films. While $SrTiO_3$ substrates have many superior properties including chemical stability in the Hg-vapor, they are expensive, only available in small area, and have poor microwave properties such as high dielectric constant and high microwave loss tangent. It is thus desirable to explore other lower-cost, large-area, and microwave compatible substrates for the growth of the Hg-based cuprate thin films. One such substrate candidate, $LaAlO_3$, is available in large area (>3 inch diameter wafer) with much lower cost and has excellent microwave properties. However, until now, only poor-quality Hg-based cuprate thin films have been obtained on $LaAlO_3$ substrates by using the same procedure as that for growth on $SrTiO_3$ substrates [6]. For Hg-based cuprate films on $LaAlO_3$, T_c's are nearly 20 K lower and J_c's are as much as one order of magnitude lower than those obtained on $SrTiO_3$ substrates. Since the chemical stability of $LaAlO_3$ is not as good as $SrTiO_3$ at high temperatures in the presence of the Hg-vapor, chemical reactions and interdiffusion near the film/substrate interface may seriously degrade the superconducting properties of the films. To reduce the possibility of the chemical reactions and interdiffusion, the high temperature Hg-vapor processing time should be as short as possible.

In the conventional annealing process previously used for Hg-based cuprates, the sample temperature is increased slowly (4-6 hours) to the annealing temperature (780-860 °C) in order to maintain phase equilibrium between the precursor and the unreacted $HgO+Ba_2Ca_{n-1}Cu_nO_x$ pellet which are sealed together in an evacuated quartz tube. Since HgO decomposes at around 500 °C, two problems can arise using this slow heating cycle. First, above 500 °C the Hg^{+2} begins to react with Ca to form $CaHgO_2$ which seriously degrades the superconducting properties of the sample. Second, the high temperature processing time (500 °C to growth temperature) is unnecessarily long which increases the problem of film/substrate interface chemical reaction and interdiffusion. In order to solve these problems, we adopted a fast temperature ramping Hg-vapor annealing (FTRA) process in which the furnace temperature is ramped to the annealing (growth) temperature within 1 to 15 minutes and the sample is annealed for 5-30 minutes at the annealing temperature. With an additional follow-up O_2 anneal at 400 °C, good-quality Hg-1223 cuprate thin films have been obtained on $LaAlO_3$ substrates. In this report we describe our results on the fabrication and characterization of such films.

SAMPLE PREPARATION

The fabrication of Hg-1223 films consists of three steps: deposition of non-Hg-containing precursor films, high temperature Hg-vapor annealing, and low temperature O_2 annealing. The precursor films are deposited using the single-target rf-magnetron sputtering technique. The sputtering target is a sintered disc of well-mixed $Ba(NO_3)_2$, CaO, and CuO powders with the nominal composition of Ba/Ca/Cu=2/2/3. The disc was sintered at 900 °C for 17 hours in an oxygen atmosphere. Substrates were mounted in the on-axis configuration to a 2-inch sputtering gun and were kept at room temperature during film deposition. Pure argon gas was used as the sputtering agent. The deposition was carried out at an rf power of 75 W and a chamber pressure of 50 mTorr for 1 to 2 hours. The deposition rates are estimated to be 200 nm/hour using data from Rutherford backscattering spectrospopy (RBS) of several thin film samples. The precursor films are amorphous and insulating and need to be annealed in a controlled Hg vapor to form an oriented superconducting phase. The Hg-vapor pressure was controlled using an unreacted $HgBa_2Ca_2Cu_3O_x$ pellet and a non-Hg-containing $Ba_2Ca_2Cu_3O_x$ pellet sealed together with the precursor film in a precleaned and evacuated quartz tube. The unreacted $HgBa_2Ca_2Cu_3O_x$ pellet was prepared by mixing HgO with sintered $Ba_2Ca_2Cu_3O_x$ powders and pressing them into a pellet. The mass ratio of the $HgBa_2Ca_2Cu_3O_x$ pellet to the $Ba_2Ca_2Cu_3O_x$ pellet is approximately 5 to 2. After Hg-vapor annealing, the samples were annealed in flowing O_2 at 400 °C for 24 hours to optimize the oxygen content.

EXPERIMENTAL RESULTS

Similar to those films on $SrTiO_3$ substrates [6], the Hg-based films grown on $LaAlO_3$ substrates were superconducting after Hg-vapor annealing with T_c's in the range of 105 to 115 K. However, the quality of the films grown on $LaAlO_3$ have poorer properties (T_c, J_c) compared to films prepared on $SrTiO_3$. After the follow-up O_2 anneal, the superconducting properties were significantly improved for the films prepared using the FTRA process compared with those prepared using the regular thermal annealing process. In addition, the volume portion of the impurity $CaHgO_2$ phase was significantly suppressed in the films annealed using the FTRA process as indicated by a microstructure analysis with the SEM and energy dispersive X-ray (EDS) spectrometer [7]. The T_c's and J_c's of the films prepared using the FTRA process are comparable to the best values obtained for the Hg-based cuprate films grown on $SrTiO_3$ substrates.

The sample structures are characterized using x-ray diffraction (XRD) using a Cu K_α radiation source. Fig. 1 shows the XRD θ–2θ pattern of a sample prepared using the FTRA process. A series of (00ℓ) peaks from the Hg-1223 phase (indexed) can be identified. In addition, (00ℓ) peaks from the Hg-1212 phase (diamonds) are also visible, which indicates that the film is a c-axis-oriented mixture of the two phases. The higher peak intensity of the Hg-1223 phase suggests that Hg-1223 is the dominant phase, which is consistent with the observed high T_c which is discussed later. The c-axis lattice constants are estimated to be 12.7 Å and 15.7 Å for Hg-1212 and Hg-1223 phases, respectively, and are consistent with those reported for bulk samples.

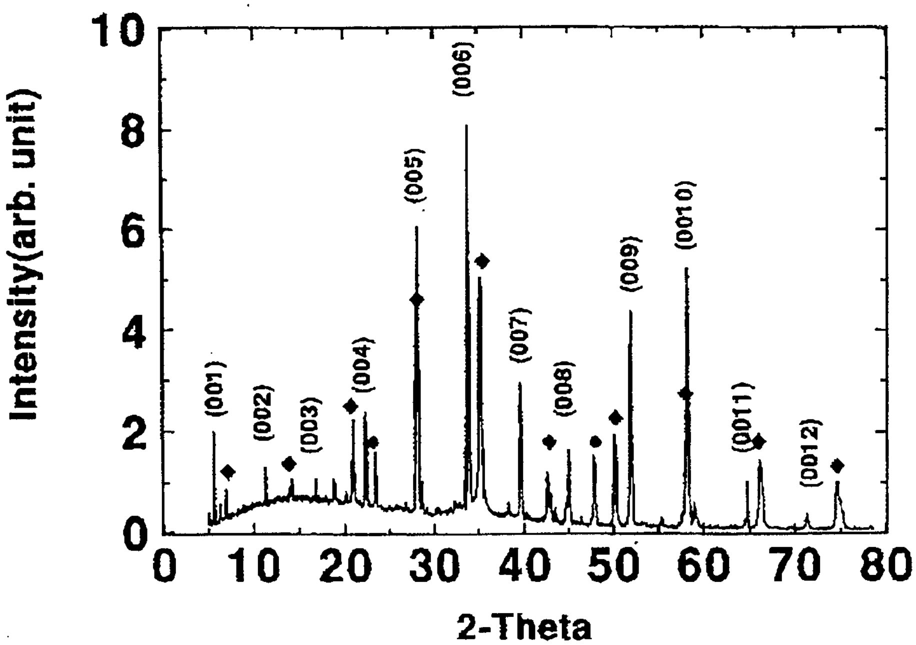
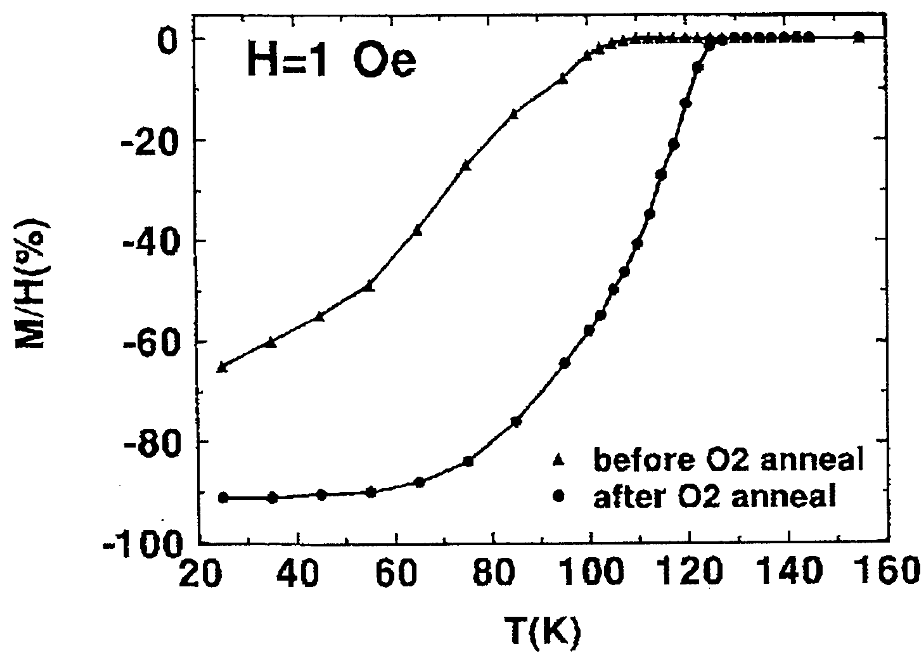


Figure 1. X-ray diffraction patterns of Hg-1223 thin films fabricated using the FTRA technique. The indexed peaks are from Hg-1223 phase. The diamond peaks are Hg-1212 phase and the solid circle peaks are the $LaAlO_3$ substrate.

The T_c for the film was determined from both magnetic and electrical transport measurements. Fig. 2(a) shows the temperature dependence of the zero-field-cooled dc magnetization (M) of a sample in a 1 Oe magnetic field using a SQUID magnetometer (Quantum Design). The field was applied normal to the film plane. As shown in Fig. 2(a), T_c is near 110 K before the O_2 anneal and is increased to 128 K after the O_2 anneal. Moreover, the superconducting transition is much sharper after the O_2 anneal. The electrical transport measurement, Fig. 2(b), of the same sample is consistent with the magnetic measurement. After the O_2 anneal, the screening effect is increased from only 60% to over 90% and the zero field cooled (ZFC) curve becomes much flatter at low temperatures. In the electrical transport measurement, most films made using the FTRA process exhibit a sharp onset of resistive transition above 130 K, but zero-resistance T_c is in the range of 124 to 128 K. In the normal state, the films display metallic linear temperature dependence with a resistivity of 180 to 300 $\mu\Omega$ cm at 300 K.

(a)



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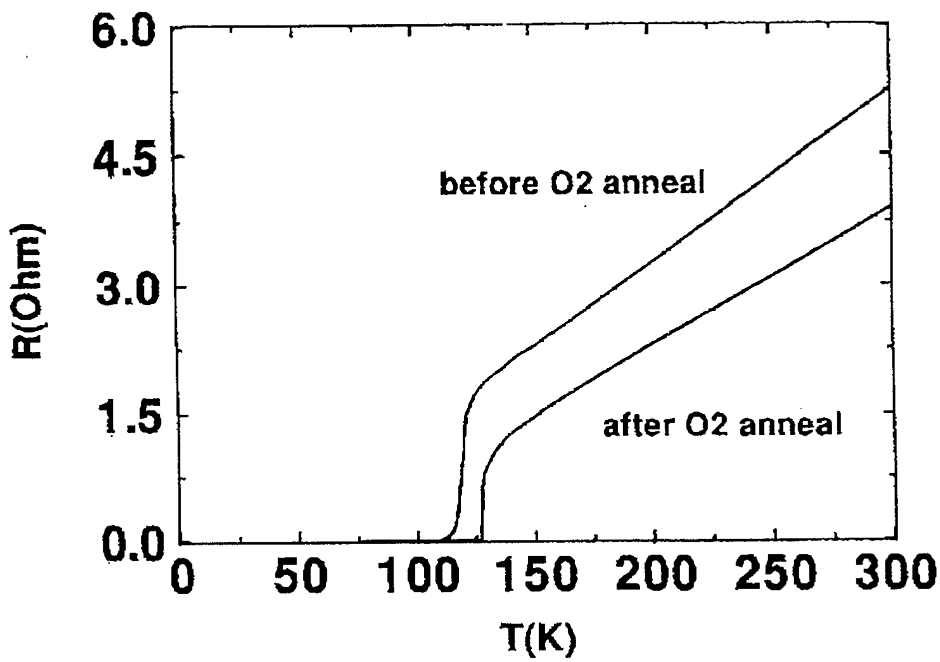

Figure 2. (a) Zero-field-cooled dc magnetization of an Hg-1223 film as a function of temperature for H=1 Oe, and (b) temperature dependence of the resistivity of the same sample before and after O_2 annealing at 400 °C.

To estimate the J_c for the film, the M-H loop was measured at different temperatures with a magnetic field applied normal to the film plane. Using the Bean model, J_c was obtained from the magnetization as functions of the magnetic field and temperature. It should be noted that in calculating J_c values, we used the sample dimensions (1.5 to 4 mm^2 and 0.2 to 0.4 μm thickness) rather than the grain size so that the measurement gives a lower bound on J_c. Most samples made using the FTRA process had fairly poor values of J_c before the O_2 anneal. Both J_c and its temperature dependence are significantly improved after O_2 annealing. Generally, the increase of J_c is 10-20% at 5 K, up to 300% at 77 K, and as high as an order of magnitude at 110 K. The temperature and field dependencies of J_c for a sample made using FTRA followed by an O_2 anneal are shown in Figs. 3(a) and 3(b), respectively. J_c at 5 K is about 1.4 x 10^7 A/cm^2 in the absence of magnetic field and over 1 MA/cm^2 in a 5 Tesla magnetic field. With increasing temperature, J_c decreases approximately exponentially which suggests a thermally activated flux creep [8] at elevated temperature. At 77 K, J_c is 1.5 x 10^6 A/cm^2, and, at 110 K, is 2.5 x 10^5 A/cm^2 at zero field. The result for one of the best Hg-1223 films on an $SrTiO_3$ substrate is also included in Fig. 3 and indicates that the quality of the Hg-based cuprate films grown on $LaAlO_3$ substrates is comparable to those grown on $SrTiO_3$ substrates [6,9].

In summary, good-quality Hg-based cuprate thin films have been fabricated on $LaAlO_3$ substrates using fast temperature ramping Hg-vapor annealing followed by annealing in O_2. These films are very promising for various microwave device applications.

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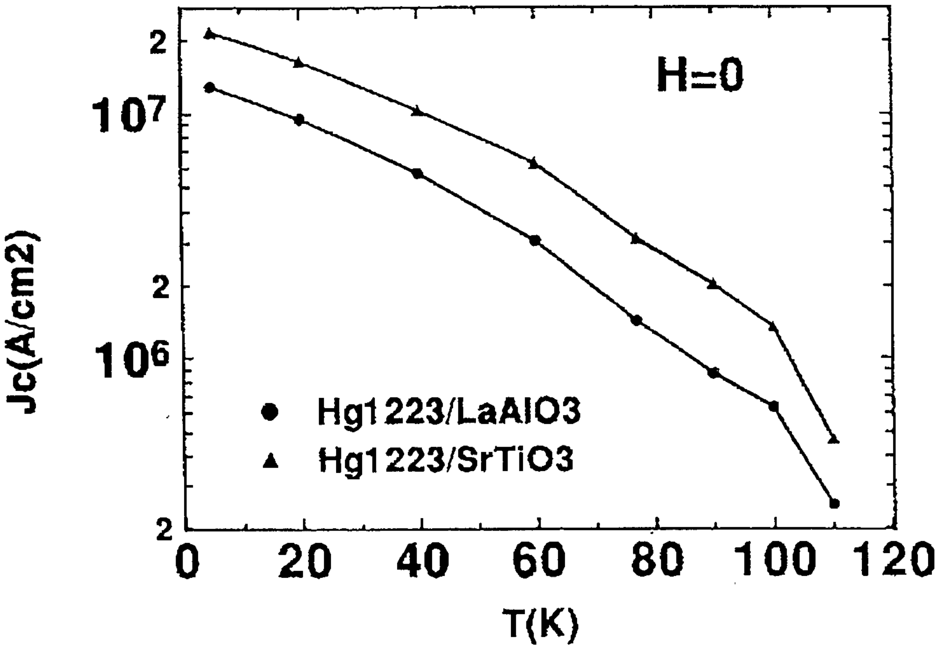
(a)



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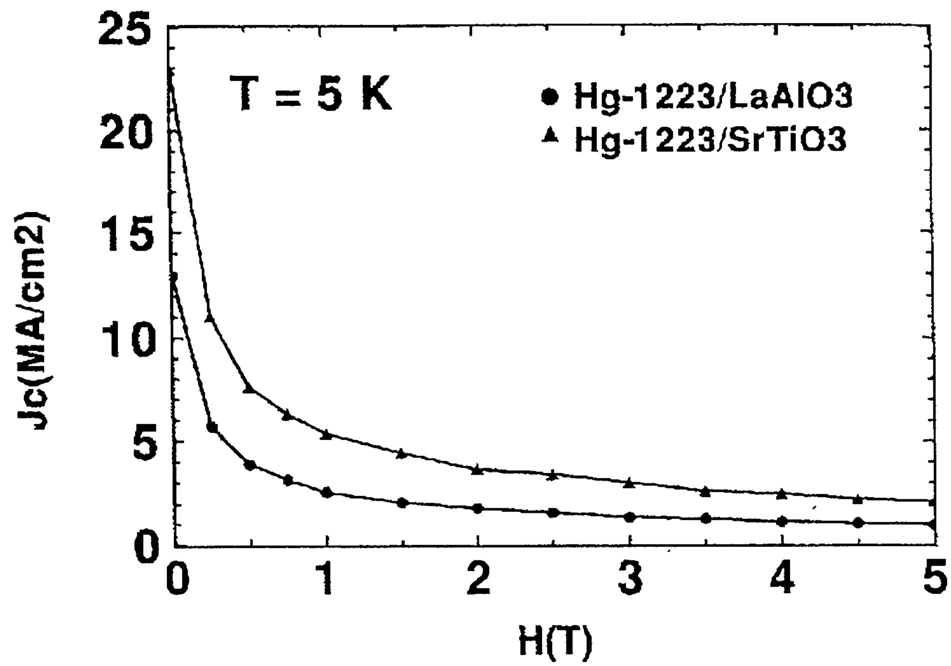

Figure 3. (a) J_c of Hg-1223 films as function of temperature and (b) as a function of applied magnetic field parallel to the *c*-axis.

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